Abstract

We evaluate the hypothesis that the reactivity trend for iodination of natural humic substances (HS) resembles that for the iodination of some substituted phenols. The hypothesis was tested by comparing the rates of reaction of I_2(aq) with HS and a series of eight substituted phenolic compounds. Rates of iodination for all of the phenolic compounds, except salicylate, are described with an empirical rate law:

$$R = k_{obs} \frac{\left[\begin{matrix} phenolic \\ compound \end{matrix} \right]^1 \left[I_3^- \right]^1}{\left[H^+ \right]^1 \left[I^- \right]^2}$$

with the values of k_{obs} related to the structure of the substituted phenol. The values of k_{obs}, corresponding to iodination of the simple substituted phenols, range from 5.6×10^{-8} to 4.7×10^{-5} Ms^{-1} at 25° C. These rate coefficients can be predicted over three orders-of-magnitude from a modified Hammett relation.

The rates of iodination of HS fall within the range measured for substituted phenols, suggesting that iodination of the natural HS proceed by similar pathways. The humic substances differ markedly in their reactivity toward I_2(aq) in several important ways. First, unlike the substituted phenols, the HS typically reacted in two stages. An initial stage involves rapid uptake of I_2(aq) and is followed by a much slower reaction. Surprisingly, each stage of the reaction follows a similar rate law with respect to the reactants. Secondly, rates of iodination of the HS are characterized by non-integer rate orders with respect to the concentration of protons and the concentration of dissolved iodide [$I^!$(aq)].